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FARADAY 1ST LAW OF GROWTH KINETICS AND CABRERA MOTT STUDIES OF ZIRCONIA

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Abstract: The Cabrera – Mott theory implies anodic polarization of zircaloy-4 is limited by the field – facilitated activated jumps of metal ions at the metal – oxide interface was originally proposed to interpret growth of thin oxide films on planar metal surfaces. The growth kinetics of zircaloy-4 have been studied at constant current densities ranging from 6 to 16 mA.cm $^{-2}$ at room temperature in order to investigate the dependence of ionic current density on the field across the zirconia. Thickness of the oxide films was estimated from capacitance data. The formation rate, faradaic efficiency and differential field were found to increase with increase in the ionic current density for zirconia. The addition of anions found to improve the growth kinetics of different colours covering entire thin films on the surface of the different anodization voltages. A plot of logarithm of anodization rate vs. logarithm of current density is fairly linear. From linear plots of logarithm of ionic current density vs. Differential field and applying the Cabrera – mott theory. The half – jump distance (a) and height of energy barrier (W) were deduced as 1.09 Å and 0.94eV.

Keywords: Anodic polarization, Zircaloy-4, electrolyte, constant current densities, Faraday 1st law and Cabrera – Mott theory.

I. INTRODUCTION

The theory advanced by Cabrera and Mott (1) on the basis of earlier work by Mott (2) to explain the rate of growth of oxide films on metals usually has been regarded as directly applicable to the case of anodic oxidation. When valve metals such as zirconium and its alloys like Zr – 2, Zr – 4, etc are anodically polarized, interference colored oxide films are formed. These smooth and mechanically perfect anodic films can act as dielectrics in capacitors. The phenomenon of anodic oxidation plays a basic role in micro-circuitry (3) and in thin film methods (4). Anodic oxide films formed on valve metals are useful in the field of electrical and electronic components (such as capacitors, resistors, dioxides and photo electric devices), corrosion protection and for decorative purposes. Applications of anodic films have been reviewed (5). Guntherschultze and Betz (6) were the first to investigate the kinetics and mechanism of the anodic oxidation of metals. The kinetics of anodic film formation on zirconium in various electrolytes has been reviewed (7). Vermilyea (8) has published data covering a range of temperatures, which dispute some of the predictions of the theory of Mott and Cabrera. Their theory predicts a logarithmic increase of forming field with current density (or rate of formation). Zirconium and its alloys have been studied for being used in the nuclear power industry and have been recently commercialized for its use in medical implants, especially for total knee and hip replacements after hydrothermally grown oxide (9). Zr and Zr alloys have greater strength, lower cytotoxicity and lower magnetic susceptibility than titanium (10). These advantageous properties make Zr and its alloys good promising candidates as materials in orthopaedic surgery.

In this research work, to study the effect of constant current densities on the kinetics of formation of oxide films on Zircaloy-4 in 0.1M Oxalic acid dihydrate by faraday 1st law and Cabrera – Mott theory to deduce the half – jump distance (a) and height of energy barrier (W).

II. MATERIALS AND METHODS

Zircaloy-4 was of 98% nominal purity, supplied in the form of plate by **Nuclear Fuel Complex, Hyderabad** as gift samples. Thinning of this Zr-4 plate was done by **Defence Metallergical Research Lab, Hyderabad**. Cutting of the thinned sheet was done at **tools and techniques, Hyderabad.** The chemical composition of zircaloy-4: 0.07 wt. % chromium; 0.23 wt. % iron; 1.44 wt. % tin and balance is zirconium.

In the present work, the foil samples used were cut with the aid of a punch into flag-shaped specimens of 1 cm2 working area on both side and 1 ½ cm long tag .The chemical polishing mixture consisted of acids such as HNO3, HF and water in a definite volume ratio of 3:3:1.

2.1 Electrochemical conditions

The counter electrode was a sheet of Platinum [11] (2x3 cm, weight 3.000 gm). The working electrode was the Zr-4 [12] sample. For anodizing, a double walled glass cell 100mL capacity was used. The experiments were performed in an electrolyte, 0.1 M Oxalic acid dihydrate. All experiments were carried out at constant current densities ranging from 6 to 16 mA.cm^{-2}. The experimental procedure for the anodic polarization by faraday 1st law is given elsewhere [13]. The kinetic results calculated are formation rate in Vs¯, faradaic efficiency (η) % from the conventional plots V vs. t, D_c vs. D_F. The Cabrera – Mott theory to deduce the half – jump distance (a) in Å and height of energy barrier (W) in eV.

III. RESULTS

3.1.1 Kinetic measurements

Specimen of zircaloy-4 was polarized galvanostatically in 0.1M oxalic acid dihydrate at a constant current density of 8mA.cm^{-2} and at room temperature. The anodization voltage vs. anodization time plot **Fig.1** was found to be linear up to the breakdown voltage. The breakdown voltage was observed to be 113V for zircaloy-4. The plots of anodization voltage vs. anodization time, reciprocal capacitance vs. time (or) thickness by capacitance (ΔDc) vs. thickness by faradaic (ΔD_F) and thickness by capacitance vs. anodization voltage for zircaloy-4 are linear up to break down voltage and plots are shown in **Fig. 1, 2 and 3.** From these plots the formation rate, faradaic efficiency and differential field were estimated and are summarized in **Table 1.**

Dependence of ionic current density on the field of formation

Anodic polarization were carried out separately in 0.1M oxalic acid dihydrate at constant current densities ranging from 6 to 16mA.cm^{-2} to investigate the exponential dependence of the ionic current density on the field across the oxide film. The plots of anodization voltage vs. anodization time, reciprocal capacitance vs. anodization time are shown in **Fig. 4 and 5.** The anodic polarized zirconia plot at 12mA.cm^{-2}, anodization voltage vs. anodization time has two linear portions intersecting at 84 volts. The potential further increased up to the breakdown voltage i.e. 152 volts. The anodic polarized zirconia plots at 14 and 16mA.cm^{-2}, anodization voltage vs. anodization time has three linear portions up to the breakdown voltage i.e. 167 & 171 volts respectively .The formation rate, faradaic efficiency and differential field were found to increase with the increase in the ionic current density for zirconia.The details are summarized in **Table 2.** The plots of log. ionic current density vs. differential field gave fairly linear relationship as shown in **Fig 6.**

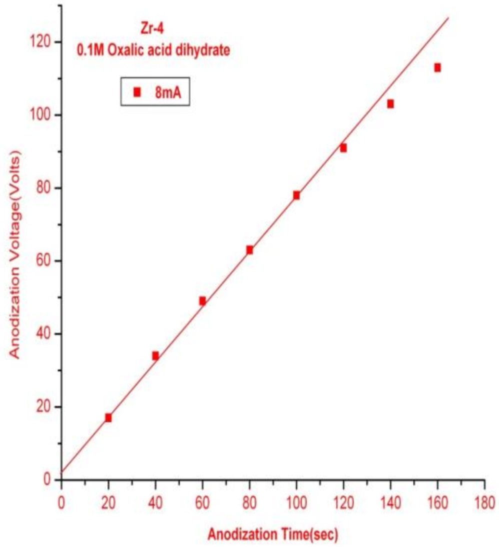

Figure. 1: Plot of anodization voltage as a function of anodization time.

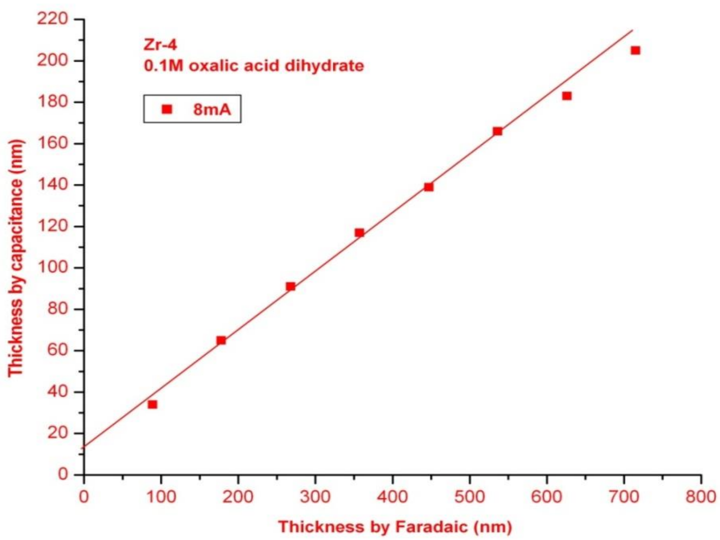

Figure. 2: Plot of thickness by capacitance as a function of faradaic.

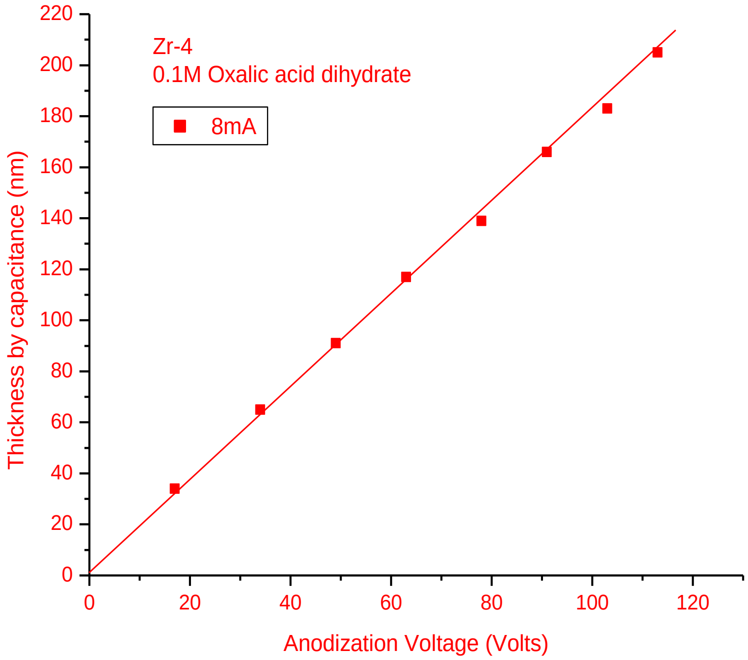

Figure. 3: Plot of thickness by capacitance as a function of anodization voltage

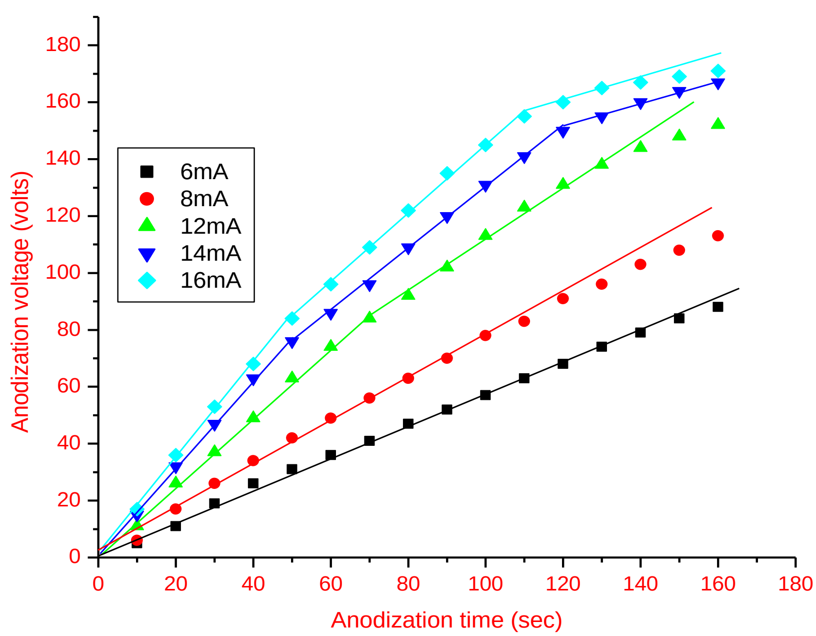

Figure. 4: plot of anodization of voltage as a function of anodization time

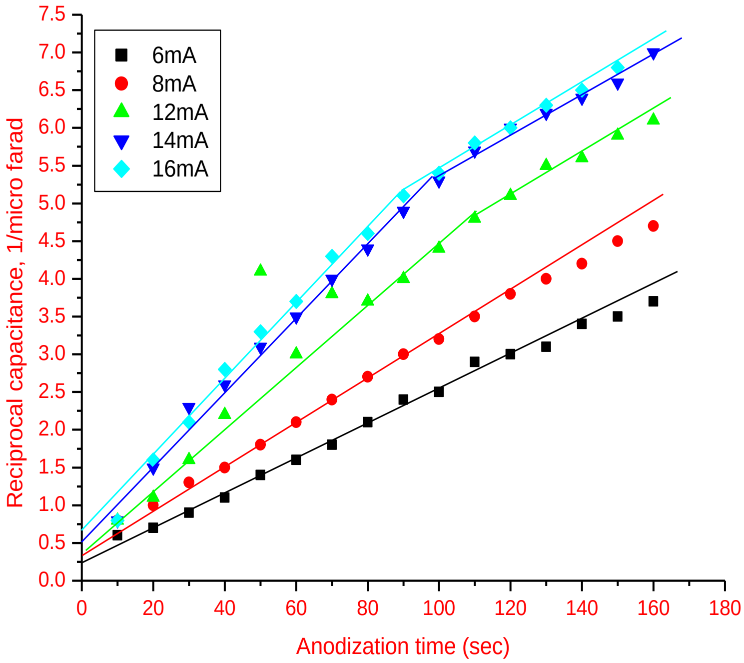

Figure.5: Plot of reciprocal capacitance as a function of anodization time

Table- 1 Anodized oxide films formed on zirconia

Current density $mA.cm^{-2}$	Formation rate $V.s^{-1}$	Faradaic efficiency η (%)	Ionic Current density $mA.cm^{-2}$	Log.ionic current density,Log.i_i	Differential field,F_D ($MV.cm^{-1}$)
6	0.65	52.02	3.121	0.4942	4.978
8	0.77	58.53	4.682	0.6704	5.452
12	1.3	65.03	7.803	0.8922	5.585
14	1.52	66.84	9.357	0.9711	5.871
16	1.67	68.25	10.92	1.038	6.543

IV. DISCUSSION

4.1. Growth kinetics

4.1.1. Ionic current density on differential field strength.

The growth kinetics involves the study of variation of differential field with the ionic current density and calculation of kinetic parameters half jump distance (a) and height of the energy barrier (W) assuming the rate determining step lies at the interfaces or within the bulk of the oxide. In the present study it was assumed that the highest energy barriers are situated at the interfaces and the Cabrera-Mott type theory is applicable. The **Fig- 3,** show the variation of log. ionic current density with differential field of formation for anodization of zircaloy-4 in 0.1M oxalic acid dihydrate, **Table-1,** illustrates the details of influence of current density on kinetic results. Applying Cabrera Mott theory, therefore using equations with n = 1.212 x 10^{15} ions / cm^2, ν = 10^{13} Hz, q= 2e for zircaloy-4 (the assumption of limiting saturation value for the concentration of active sites for the anodic oxide growth at a surface), the kinetic parameters of high field ionic condition are deduced and summarized in **Table - 2.**

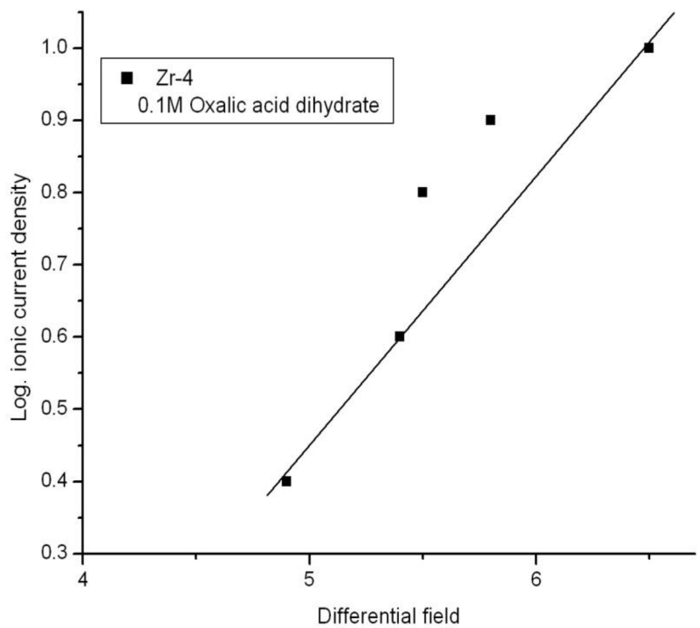

Figure. 6: Plot of variation of log. ionic current density with differential field.

Table- 2: Estimates of kinetic parameters of high field ion conduction

(Control by Oxide / Electrolyte barrier) of zirconia.

Electrolytes	A_i mA.cm^{-2}	B_i cm.V^{-1}	W eV	a Å
0.1 M OAD	4.58	0.85	0.94	1.09

The value of half-jump distance 'a' deduced in electrolyte for zircaloy-4 is larger than the mean separation of oxygen ion in ZrO_2, 1.66Å. However, the value of 'a' is comparable to the half lattice parameter of for the cubic modification of ZrO_2. The low value of 'a' found in the case of oxalic acid dihydrate could probably be , due to the migration of oxygen ions via interstices, grain boundaries etc., in which case the mean jump distance could be more than the inter atomic distance. The value of 'A_i', 'B_i', 'W' and 'a' deduced for zircaloy-4 in 0.1M oxalic acid dihydrate are found to be nearly same. The kinetic parameters obtained in the growth kinetics, in the electrolytes studied using zircaloy-4, it was found that the composition and crystalline structure have marked influence.

V. CONCLUSIONS

Anodic oxide film formation in the electrolyte 0.1M oxalic acid dihydrate found to improve the kinetic results, formation rate, faradaic efficiency and differential field with the current density. The addition of anions found to improve the growth kinetics of different colours covering entire thin films on the surface at different break down voltages. On the basis of the evidence available the rate determining step is considered to be situated at the oxide/electrolyte interface, and Cabrera- Mott theory is applied to the growth kinetics, the deduced value of half jump distance (a) height of the energy barrier (W) are found to be 1.09Å, 0.94eV respectively.

VI. ACKNOWLEDGEMENTS

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